

DISSOLVING COAL AT MODERATE TEMPERATURES AND PRESSURES

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Introduction

The objective of the research reported here was to determine the kinds and proportions of breakable C-C and C-O bonds in the connecting links between the condensed systems in coal. Such information should tell us about the possibility of coal liquefaction under mild conditions. The kinds and proportions of C-O and C-C bonds were investigated by cleavage reactions. Cleavages of C-O bonds in esters and ethers by strongly basic amines, iodides, and acids are discussed first and then our results on the distribution of oxygen in coal are compared with the results of other workers. We then discuss the cleavage of C-C bonds in connecting links by oxidations of coal fractions and some differences among the oxidation products. In terms of C-C bonds to be broken by oxidation, the principal problem is determining whether the condensed aromatic systems are joined by single or multiple methylene groups. Our conclusions are compared with some in the literature. This paper is an expansion of a previous presentation.(1)

The above findings and conclusions are the foundation for a new program to prepare a coal product on a laboratory scale at a moderate temperature and pressure that will melt or dissolve in a cheap solvent at or below 100°C. Ash can then be removed and the product can be used as a clean fuel or processed more easily than coal to a liquid fuel. A progress report will be made.

Coal Preparation: Extraction of Coal With Pyridine

All of the work reported here was done with a beneficiated Illinois No. 6 coal, obtained from Pennsylvania State University as PSOC 25. This dried coal contained 76.0% C, 4.88% H, 1.46% N, 2.17% S, 1.71% ash, and 13.8% O by difference. Much of the work reported in this section was carried out with soluble coal fractions so that changes could be followed by number-average molecular weights (\bar{M}_n). Some of these fractions were prepared by extracting our coal exhaustively with pyridine at 100°C. About 16% dissolved, apparently without chemical reaction. About one-third of the pyridine-soluble material was soluble in toluene; it contained more hydrogen and less oxygen than the toluene-insoluble, pyridine-soluble (TIPS) fraction, which is a useful model for coal and was used in much of our work. The TIPS fraction is heterogeneous in molecular weight and chemical composition. One TIPS fraction of \bar{M}_n 1100 (by vapor-phase osmometry) was fractionated by GPC; 76% of the total had \bar{M}_n in the range 550-1550. After hydrolysis of a TIPS fraction by alcoholic KOH, the products were easily separated into fractions of \bar{M}_n 350 to 1430, H/C ratios (a measure of aromaticity) of 0.98-0.74, and with different proportions of aromatic hydrogen.

Reactions of Coal Fractions With Amines

Strongly basic amines have long been known to dissolve more coal than pyridine.(2,3) We now attribute the high solubilities of coals in these solvents to chemical cleavage of C-O bonds in ester and ether groups. This conclusion comes from reactions of both TIPS and pyridine-extracted coal with BnNH_2 . After these reactions, most of the free BnNH_2 was removed by vacuum distillation and the rest by washing with dilute aqueous HCl; the latter was then extracted by aqueous ammonia. Table 1 shows that close to one molecule of BnNH_2 becomes bound to the TIPS for each cleavage reaction or additional molecule formed. With both TIPS and pyridine-extracted coals, the extents of reaction increase with the severity of treatment. For the pyridine-extracted coal, we do not know how much BnNH_2 is incorporated per cleavage, but if the ratio is 1, there is about 350 in molecular weight units associated with each bound BnNH_2 .

The amine extracts from long reactions of coal at 100° are apparently true solutions, but they become partly insoluble on drying. Thus, one EDA extract was

centrifuged and dried at 76° and 1 torr, but then only 90.5% was soluble in EDA and only 24% was soluble in pyridine on repeated extractions. In a BnNH_2 extraction, considered to be equivalent, the extract was centrifuged in an ordinary centrifuge. Another 1.5 hours at 30,000 g then produced no additional precipitate. Nearly all the solvent was then removed from the solution and 200 mL of pyridine was added to a 1-g sample. The total solubility in Table 2 is consistent with other extractions but the high solubility in pyridine was unprecedented. We think that this high solubility is due to the omission of the first drying, but the presence of a few tenths of 1% of BnNH_2 in the pyridine may also have had some effect. The drying may partly reverse the cleavage or cause condensation in other ways.

Other Cleavage of TIPS

Several other reagents, mostly halides or sources of halogen, but also acids and sodium, also cleave TIPS, presumably at C-O bonds as reported at the Houston meeting.(4) Table 3 gives the average numbers of molecules recovered from an original TIPS molecule, as measured by \bar{M}_n . After allowance for bound halogens, the carbon recoveries were usually 90-95%. We assume that the missing material was low molecular weight water-soluble or volatile material lost in the workup and therefore that the numbers in Table 2 are minimum values. However, to the extent that the products contain salts or other impurities (for which we have no evidence), the numbers in Table 2 are too large.

A TIPS fraction of \bar{M}_n 1283 was treated for 7-15 days at 90°C with hydrogen iodide in solution in pyridine, toluene, or water. By GPC, the high-molecular weight peak in the TIPS disappeared almost completely and was replaced by low molecular weight peaks. Similar but incomplete changes occurred in toluene and water. The reaction of HI in pyridine resulted in recovery of 4.4 moles of product per 1283 g of TIPS and incorporation of 3.03 g-atoms of iodine per initial mole of TIPS. From the iodine content of the product, we would expect 4.03 molecules of product, in good agreement with the \bar{M}_n data considering that there was 6% loss of carbon and that the iodide hydrolyses at room temperature.

Distribution of Oxygen in a TIPS Fraction

A TIPS fraction of \bar{M}_n 1090, by reaction with alcoholic KOH, contains ~ 0.8 ester group per average molecule and reaction with HI or ZnCl_2 gives ~ 1.2 additional cleavages per TIPS molecule. The phenol content corresponds to 3.5 oxygen atoms per average molecule. The net result is that these three functional groups account for 64% of the 14.4% oxygen in our coal. These results are compared with results of others in Table 4. The principal difference is that we report as esters what others report as carboxyl groups.

Although there is little doubt about the cleavage of ethers by hydrogen iodide, or of esters by amines, the cleavage of ethers by EDA and BnNH_2 has no precedent in the literature. We have treated model ethers with these amines for long periods at 100°C, sometimes in the presence of an equal weight of coal, but we have found no evidence of reaction with benzyl phenyl ether, dihexyl ether, 4-hexyloxyphenol, or trimethylene oxide. However, since the amines and the halides produce similar effects, we see no alternative to ether cleavage by amines. Perhaps the involvement of condensed aromatic nuclei or the uneven concentration of phenol groups(9) makes the coal ethers more reactive.

Oxidations of Coal Fractions

We reported most of our work on coal fractions at the Atlanta Meeting.(10) We aimed at maximum recovery of "black acids", slightly soluble in weak aqueous base, with minimum loss of carbon. We expected investigations of these black acids, made with different oxidizing agents, to give us information on breakable C-C bonds in coal. For oxidations, we used mostly extracted coals in suspension, and aqueous NaOCl or oxygen in water at pH 13, adding sodium hydroxide to maintain the pH, or a suspension in 15-35% nitric acid. We obtained 65-80% yields on carbon of black acids with the reagents named, with \bar{M}_n about 1000, and 12-20% loss of carbon. Five to 10% yields of water-soluble acids were also obtained. Although the nitric acid

oxidation products had the lowest H/C ratios (0.65 from 0.73 in pyridine-extracted coal) other differences among the black acids were not obvious.

Because the yields of black acids with the three main oxidizing agents were similar, we have compared the black acids with respect to molecular weight distributions and water solubility. We used both gel permeation chromatography (GPC) in dimethylformamide and high performance liquid chromatography (HPLC), starting the elution with 10 mL of 25% n-propanol in water, followed by neat DMF. GPC was done in a Waters column with 500 Å pores, packed in DMF. HPLC separations were done on a Hamilton PRP-1 column. With each column, the flow rate was 1 mL/min and a UV detector at 313 nm was used. Several known compounds were tested on the HPLC column: 2-naphthoic acid, trimellitic acid, pyromellitic acid, and phenyl benzoate eluted at 8-12 mL but everything else tested (mostly aromatic hydrocarbons, some with one oxygen atom) eluted at 24 mL or more. Thus the HPLC column is mostly a test for water solubility. The plots of UV absorption against retention time consist mostly of fairly sharp peaks with little absorption between well-separated peaks.

Results on 11 black acids are summarized in Table 5 arranged according to their origins. Several black acids from NaOCl oxidations of pyridine-extracted coal were combined, dissolved in dilute base, and fractionally precipitated by addition of hydrochloric acid. Sample F28D precipitated between pH 5.5 and 5.0, F29E between 5.0 and 4.66. As expected, by GPC 28-D contained more of the highest molecular weight (lowest retention volume) component at 5 mL and less of the lower molecular weight materials. Sample F29E suggests that the 5.0 mL GPC peak corresponds to the 4.3 mL HPLC peak, but the correspondence is poor with Sample F29D. We suspect that the 5.0 mL GPC peak is not as homogeneous as it appears and that the water-soluble components are polycarboxylic acids that are associated in DMF.

The 5.0 mL GPC component is the major GPC component in most of the black acids in Table 5. Exceptions are black acids T74B, U60B, and U85A, which show that degradations by sodium hypochlorite, 50% nitric acid, and Ce^{4+} are relatively severe. The most 5.0 mL component came from an oxidation with oxygen in water suspension at pH 13 and 50°C; this reagent is apparently the mildest and most selective of those that we have used. However, 35% nitric acid gave more lower molecular weight and water-soluble material without much sacrifice of carbon recovery.

By HPLC, five of the eleven black acids gave at least 46% of the 4.3 mL component and seven of the eleven have a 27.8 mL component that is either the largest or second largest component. Six of the black acids in Table 3 contain more than 70% of one component by either GPC or HPLC (underlined in the Table); two of them show more than 70% of one component on both columns. One of the latter black acids, T10B, represents 68% recovery of carbon in the coal fraction. Because of our high recoveries of soluble carbon and the different effects of oxidizing agents on the aliphatic and aromatic portions of coal, these chromatographic methods offer considerable potential for determining some average structures in unprocessed coal.

Oxidations with m-Chloroperbenzoic Acid (MCPA)

The objective of this work was to determine the proportion of single methylene groups as connecting links between condensed systems in coal. This problem evolved into a search for diaryl ketones in the black acid oxidation products of coal fractions. The diaryl ketones were expected to react with MCPA to convert them to esters, which were then saponified. The critical measurement is a decrease in \bar{M}_n on saponification of the esters. However, we could measure the \bar{M}_n only on the water-insoluble products that we recovered from the saponification; the water-soluble products were presumably the lowest molecular weight material. In three out of four experiments deserving consideration, there was a 2-9% increase in \bar{M}_n of the recovered acids. In one experiment, there was a decrease in \bar{M}_n from 410 to 391, but these black acids represent only 18% of the carbon in a TIPS fraction that was oxidized with 50% nitric acid. We propose that this oxidation concentrated diaryl ketones in the black acids, but even then, their proportions were barely measurable by our MCPA method.

These results indicate that there are no important proportions of bridging methylene groups in our coal, but our method is insensitive. However, the next section shows that this conclusion is consistent with most of the evidence from the literature.

Cleavages in Diphenylalkanes

Literature data on breakdown of α,ω -diphenylalkanes are summarized in Table 6. These hydrocarbons are designated by the number of methylene groups that they contain. The first reference shows that with AlCl_3 and H_2 at 325°C , 1,3-diphenylpropane is most reactive, followed by diphenylmethane and diphenylethane. All the hydrocarbons with 0 to 4 methylene groups were cracked; the extents of reaction ranged only from 32 to 83%. The second reference indicates that 1 has the most reactive bond in coal because a very small yield of dihydroxydiphenylmethane, in which both aryl- CH_2 -aryl bonds were broken, was obtained. However, all the other references in Table 5 indicate that in the absence of AlCl_3 or BF_3 1 is the least reactive of these hydrocarbons and that there may not be much of this kind of bond present in coal anyway. Two references indicate that ether links break more easily than C-C bonds. In terms of bond energies, the phenyl-C bonds are strongest. In terms of our project objective, the C-C bonds that are breakable in conventional coal liquefaction appear to be mostly, perhaps entirely, in sequences of two or more methylene groups.

Summary and Conclusions

We have shown that 44% of the carbon in our beneficiated Illinois No. 6 coal can be dissolved by cleavage of ester and ether links by amines, acids, or iodides at 100°C and atmospheric pressure. Up to 80% of the remaining carbon can then be made soluble in weak aqueous base by oxidation at 60°C or below. One practical problem in coal liquefaction is now to try the use of cheaper reagents to break ester and ether links, and to determine what temperatures and pressures are required. Other practical problems are to reduce the consumption of base in oxidations with oxygen (pH 13 has been required) and to see if oxygen can replace part of the sodium hypochlorite or nitric acid used for oxidations. Some remarks on our progress are expected to be made at the meeting.

Acknowledgement

All of the work described here was supported by the U.S. Department of Energy through the Pittsburgh Energy Technology Center. The results reported here were supported by Contract No. 22-81ET11423.001 and the work in progress is supported by Grant No. DE-FG22-82PC50788.

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Table 1

REACTIONS OF ILLINOIS NO. 6 COAL WITH EXCESS BnNH_2

Pyridine extraction \rightarrow 18.1% sol. + 81.9% insol.

TIPS (toluene-insol., pyr.-sol.), yields corrected.

	% N	\bar{M}_n	Moles/1090g TIPS	TIPS BnNH_2
No extraction	1.68	1090	1.0	0
24 h at 23°	2.79	534	2.0	1.1
9 d at 100°	3.31	379	2.9	1.7

Pyridine-insoluble, yields corrected (%N)

4 h at 23° \rightarrow 1.3% sol.(4.36) + 97% insol.(3.49)

16 d at 23° \rightarrow 7.3% sol.(4.12)

11 d at 100° \rightarrow 45.7% sol.(5.11)+ 52% insol.(5.13)

Table 2

EXHAUSTIVE EXTRACTION OF ILL. 6 COAL
BY BnNH_2

Carbon recoveries
after correction
for bound amine

Soluble in pyridine	42.7%
Soluble in BnNH_2 , not in pyridine	1.5
Undissolved	54.2
Unaccounted for	1.6

Table 3

MOLECULES FORMED BY CLEAVAGE OF ONE MOLECULE TIPS
(mostly in pyridine solution)

Reagent	Molecules	Reagent	Molecules
ZnCl ₂	3.1	p-C ₇ H ₇ SO ₃ H	1.6
LiI·H ₂ O	3.1	Na in NH ₃ + BuNH ₂	1.6
ZnBr ₂	3.0	Me ₃ SiI	1.5
Pyridine·HI	2.7	LiClO ₄	1.4
MeI neat	2.0	HBr	1.3
Benzylamine	1.8	I ₂	1.1
BnMe ₃ N ⁺ I ⁻	1.7		

Table 4

OXYGEN DISTRIBUTIONS IN COALS

Coal	%C	daf	%O	Distribution of O, %					Ref.
				OH	C=O	CO ₂ H	Ether	Inert	
A	79.4	12.5	48	13	6	18	14	} Blaumik HI 1962, 5	
B	83.0	8.4	50	6	2	26	16		
C	88.0	4.0	30	5	0	40	25		
K-I	78.2	15.1	16	4	5	8	67	} Wachowska OH change 1977 6	
K-II	81.1	11.7	11	4	4	5	76		
K-III	87.0	6.0		4	6	25	65		
K-N	87.9	4.5		8	8	61	23		
A	92.6	4.2			5	28	67		
Canadian	89.4	3.9	24		8	48	20	Wachowska 1979 7	
Ill. 6	82.5	6.7	36	6	10	42	6	Ruberto 8	
Subbit.	77.3	16.2	35	6	27	6	26	1978	
Ill.	76.0	14.4	36	ester	16	12	36	This paper	

Table 5

FRACTIONATIONS OF BLACK ACIDS BY GPC AND HPLC

Black Acid No.	Origin	Yield ^a	Retention Times, min. ^b							
			GPC				HPLC			
T74B	TIPS	NaOCl	74	10.0 45	12.1 28	5.0 27	27.7 54	3.5 18	4.5 14	
T57B	EDA extract		43	5.1 37	7.7 20	8.1 16	23.7 81	4.8 3	4.3 2	
F28D	Pyr-extd. ^c			5.0 88	10.4 10	6.4 2	4.3 46	25.0 28	5.6 7	
F29E	Pyr-extd. ^d			5.0 74	6.8 9	7.0 8	4.3 71	27.9 25	31.1 3	
T33B	EDA-extd.		62	5.0 56	9.5 41	12.3 3	25.6 53	4.0 27	28.2 6	
R56B		O ₂ in H ₂ O		5.0 90	7.1 5	9.9 3	24.9 33	3.8 22	4.1 22	
T10B	EnNH ₂ -extd.		68	5.0 76	11.0 13	8.2 8	4.3 75	27.6 19	31.0 2	
L23B	Pyr-extd.	15% HNO ₃	68	4.8 77	7.9 18	9.7 3	27.8 51	3.9 23	29.0 18	
K23A		35% HNO ₃	64	5.0 53	7.7 32	10.0 15	4.3 62	27.9 36	31.0 2	
U60B	EDA-extd.	50% HNO ₃	18	8.1 61	10.5 25	9.7 7	4.6 58	28.0 38	31.1 3	
U85A	TIPS	Ce ⁴⁺	54	8.2 58	5.2 20	10.7 17	25.7 40	4.3 34	6.0 9	

^a Yield of black acid from indicated substrate, on carbon.

^b The numbers on the second lines for each retention times are the percentages of the total products, as measured by an ultraviolet detector.

^{c, d} Combined black acids from NaOCl oxidations precipitated between pH 5.5-5.0^c or 5.0 to 4.66^d.

Table 6

CLEAVAGES OF $\text{Ph}-(\text{CH}_2)_n-\text{Ph}$

Reagent	Temp., °C	Order of reactivity for n values	Reference
$\text{AlCl}_3 + \text{H}_2$ in C_6H_6 , 90 m	325	$3 > 1 > 2 > 4 > 0$	Taylor, ¹¹ 1980
$\text{PhOH} + \text{BF}_3$	100	1	Heredy, ¹² 1981
Tetralin, 18 h	400	$3 > 2, 4$	Benjamin, ¹³ 1978
Tetralin + H_2 30 m	450	$2 > 1$	Vernon, ¹⁴ 1930
Excess tetralin	450	$2 > 4 \gg 1$	Gronauer, ¹⁵ 1979
Decalin + $\text{H}_2 \pm$ Ph_3SnCl , 1 h	<400 450	mostly ether splits $2, 3$	Kuhlmann, ¹⁶ 1981
^1H NMR		No significant amount of 1 in THF-soluble products	Liotta, ¹⁷ 1981
$\text{CO} + \text{H}_2\text{O}$, 1 h	400	$3 > 2 > 1$ Ethers split more easily	Takemura, ¹⁸ 1981

APPLICATION OF CROWN ETHERS AS PHASE TRANSFER CATALYSTS
IN THE ELECTRON TRANSFER REACTIONS OF COAL

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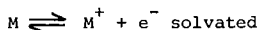
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INTRODUCTION

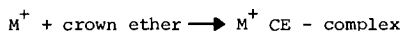
The electron transfer reactions of coal as exemplified by the Sternberg procedure (1) for reduction and reductive alkylation has been the subject of intensive investigation by a number of research groups (2-5). The reaction suffers from the problems of extended reaction time, side reactions, incorporation of the electron transfer agent and/or solvent into the coal. Further, in most cases, negligible quantities of soluble products were obtained on quenching the reaction immediately after the electron transfer step.

In view of this, the discovery by Pedersen (6,7) that certain macrocyclic polyethers called crown ethers have the ability to complex alkali metal cations, and the results of Dye (8), Kaempf (9) in the solubilization of alkali metals using these crown ethers, prompted us to envision the use of crown ethers to act as phase transfer catalyst in the electron transfer reaction with coal.

Thus, a stable solution of electrons can be prepared in an inert ethereal solvent like THF at room temperature because the equilibrium



is shifted to the right by the complexation equilibrium



The limitations of solubility, decomposition problems, reactivity and incorporation of the electron transfer agent can be overcome.

Another important facet of the crown ethers is that they have been successfully employed as reagents for direct solid-liquid phase transfer reactions (10). Thus, the problem of interphasic electron transport from solution to the aromatic substrate in coal would be solved, because the crown ether can function as a phase-transfer catalyst.

Further, the complexation of K by crown ether results in the metal cation being held inside the cavity of the crown ether and the resulting ion pair is loose. This would promote the irreversible electron transfer with bond cleavage (11).

EXPERIMENTAL

Coal: The Illinois No. 6 coal from the Burning Star No. 2 mine (courtesy of the Southern Company Services, Inc.) C-68.25%, H-5.30%, N-1.69%, S-3.62%, Ash-17.7% was used in the studies. It was demineralized, (12) extracted with Benzene:Methanol (3:1) to remove the trapped organic, and dried in vacuum at 100°C for 24 hours before use.

Reagents: The crown ether selected for study was the 18-crown-6, 1. This crown ether has a hole 2.6-3.2 Å in diameter. The electron donor alkali metal selected for the study was potassium because its ionic diameter is 2.66 Å and should, therefore, fit nicely in the crown ether hole resulting in a 1:1 complex. Using a 1:1 molar ratio of potassium to crown ether (CE), a 0.14 molar and 0.28 molar solution was prepared which was deep blue in color clearly indicating the presence of 'solvated electrons' in solution. This was reacted with different weights of coal under a blanket of nitrogen and the reaction quenched with water.

RESULTS AND DISCUSSION

Analysis: The percent g-atom of potassium consumed in the reaction of the K-CE reagent with coal was determined by measuring the difference in the volume of hydrogen evolved when the blank reagent and the reaction mixture was quenched with water after the same reaction period. To establish the accuracy of our analytical method and the validity of our reagent as an electron transfer agent, it was reacted with standard compounds and the mole of compound consumed per g-atom of potassium computed by the hydrogen evolution method. The values obtained compare favorably with those reported in literature (13) for the same compound using a different electron transfer agent and a different analytical method (Table 1).

TABLE 1

<u>Compound</u>	<u>Mol of Compound Required per g-atom of Metal</u>	<u>Literature Value</u>
Benzil	0.6	0.50
2-Butanol	1.29	1.1
Naphthalene	0.58	0.50

Effect of Electron Concentration and Time: The percent g-atom of potassium consumed in the reaction is a measure of the uptake of electrons by the coal resulting in the formation of the coal radical anion which undergoes cleavage at the ether and sulfur linkages. In the reaction of a 0.14 molar solution of K in THF with different weights of coal, the metal consumption increased with coal weight until it levelled off at the larger coal weights (Fig. 1).

One can deduce from this that for a given molar solution of metal, there is a certain concentration of electrons present which is going to be dependent on the amount of crown ether used. As the coal weight increases, the aromatic substrates available for electron transfer increases and more electrons are transferred to coal which is reflected in the amount of K consumed. This will continue till at a certain coal weight, all the available electrons get transferred. Any further increase in coal weight will still reflect the transfer of all the available electrons and the K consumed will be the same in each case. For the 0.14M solution, the minimum weight of coal required to be able to take up all the available electrons is 100 mg.

Increasing the K concentration to 0.31 molar showed a dramatic increase in the percent K consumed (Fig. 2) although the plot of percent K consumed against coal weight followed the same pattern as that obtained for the 0.14 molar solution. It is probably that at this increased electron concentration, a two electron transfer is taking place with the formation of the coal dianion and at the lower concentration, a one electron transfer occurs with the formation of the radical anion (Scheme 1).

Since complete electron transfer takes place at the 100 mg coal weight, it was selected for a time study. The K consumption increases very rapidly in the first thirty minutes and then levels off (Fig. 2). This suggests that the transfer of electrons proceeds very rapidly and is complete in thirty minutes with the electron concentration obtained from a 0.14M K/THF solution.

Solubility Studies: Based on the above studies, 1 g of coal was treated with 20 mmol of K in the THF with 20 mmol crown ether (0.2 molar in K), stirred for six hours and quenched with water. After rotaevaporating to dryness, the reacted coal was washed extensively with water to remove the K-salts and crown ether and extracted with THF. The degree of conversion was calculated as % solubility = wt of feed coal - wt of THF insoluble residue/wt of feed coal x 100. The elemental analysis and solubility of the feed coal and solubilized coal is summarized in Table 2.

TABLE 2

Sample	C	H	S	N	*THF		
					Solubility	H/C	O (By diff)
Feed Coal	74.47	4.97	3.55	1.42	5.9%	0.8	15.59
Reacted Coal (1 g Coal/ 0.2M K-THF Solution)	74.41	7.39	2.0	1.40	52.%	1.12	14.80

*Based on coal residue insoluble in THF. Thus any error in the weight due to presence of moisture crown ether, etc., would only mean more THF solubility than obtained.

^1H and ^{13}C NMR Studies: The 470 MHz ^1H NMR spectrum of the solubilized coal is shown in Fig. 3, while the proton decoupled ^{13}C NMR spectrum is shown in Fig. 4. The integration in the ^1H NMR shows that the ratio of $\text{H}_{\text{ar}}:\text{H}_{\text{sat}}$ is 1:4. The broad peak around 3.4 ppm is assignable to the hydroxyl protons. The sharp resonance signals in the 1-1.6 ppm region are assigned to the $\text{R}-\text{CH}_2-\text{R}$ grouping. These could also arise from methyl protons (CH_3-R), however, the absence of any methyl carbon resonances in the 11-22 ppm region rules out this possibility. Furthermore, the appearance of a group of signals in the 28-34 ppm region confirms the presence of methylene groups ($-\text{CH}_2-$) in a saturated ring system. This, in all probability, would be a saturated six-membered ring system joined to an aromatic ring system. The strong resonance signal at 69.7 ppm evidently comes from the C atom bearing the hydroxyl group ($-\text{CHOH}$) in the saturated ring. The aromatic ring carbons appear in the 125-145 ppm region. The 125-128 ppm signals are due to the protonated aromatic carbons and the 138-145 ppm signals due to quaternary naphthalenic type carbons.

Thus, by using a phase transfer catalyst 18-crown-6, rapid and effective electron transfer to coal has been achieved. This has resulted in the formation of coal radical anions or dianions depending on the concentration of the solvated electrons in solution (Scheme 1). These ions have undergone facile cleavage reactions (Scheme 2) resulting in depolymerization as demonstrated by the considerable increase in THF solubility from 5.9% for the starting coal to 52% for the reacted coal. The increase in the H/C ratio from 0.8 to 1.12 representing an uptake of 32H atoms per 100 C atoms is due in part to hydrogen pick-up from the capping of the cleavage coal radical or anion fragments. That this corresponds to reductive cleavage of the ether bonds in coal is supported by the presence of a large percent of hydroxyl groups in the solubilized coal as indicated by ^1H NMR. A Birch type reduction of the aromatics to hydroaromatics would account for the uptake of the remaining hydrogen atoms (Scheme 3) and is supported by the appearance of the $\text{R}-\text{CH}_2-\text{R}$ grouping in both the ^1H and ^{13}C NMR.

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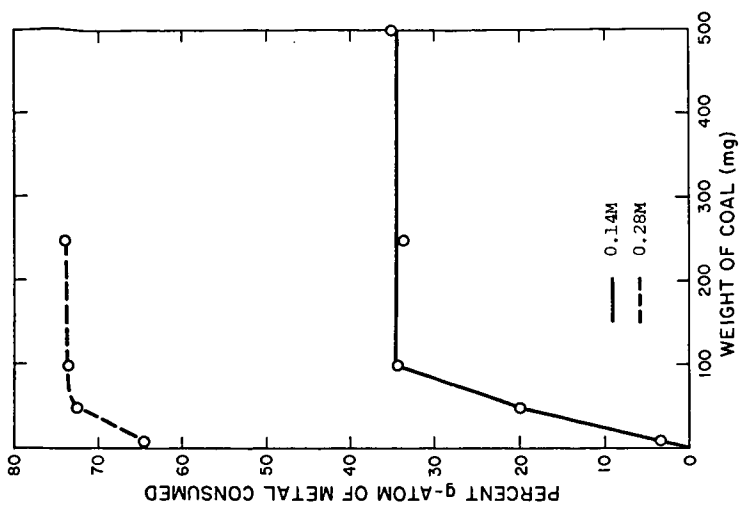


Figure 1.

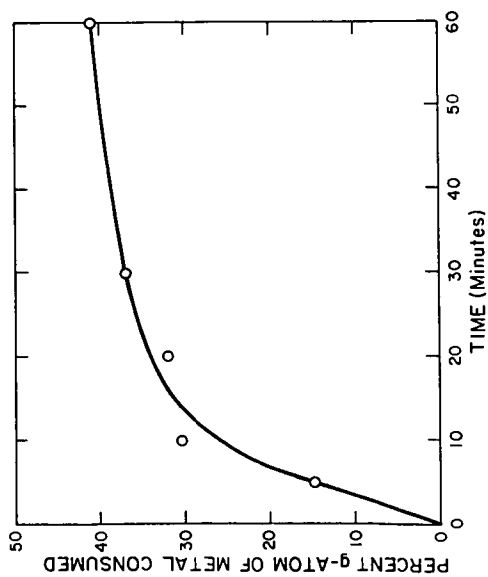


Figure 2.

Figure 4.

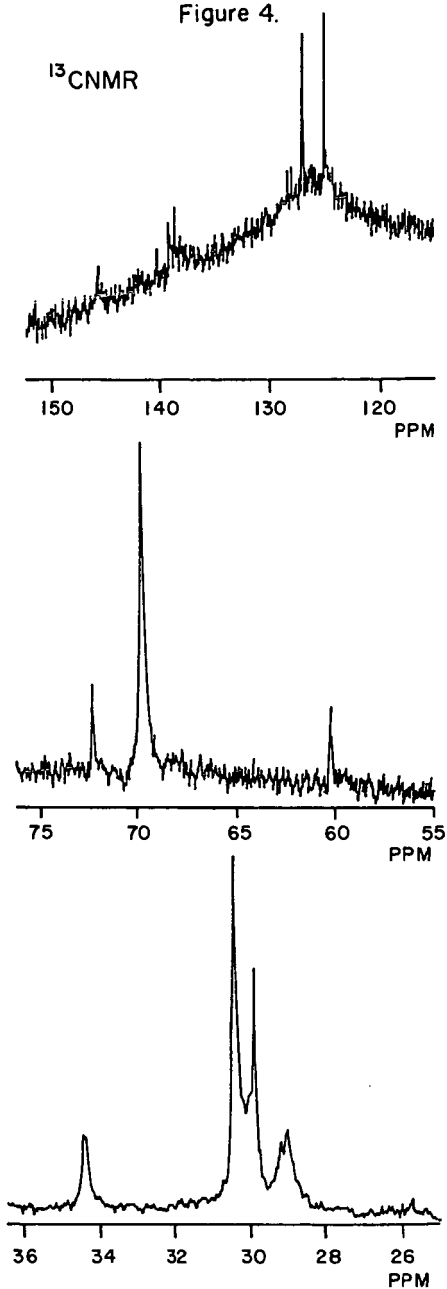
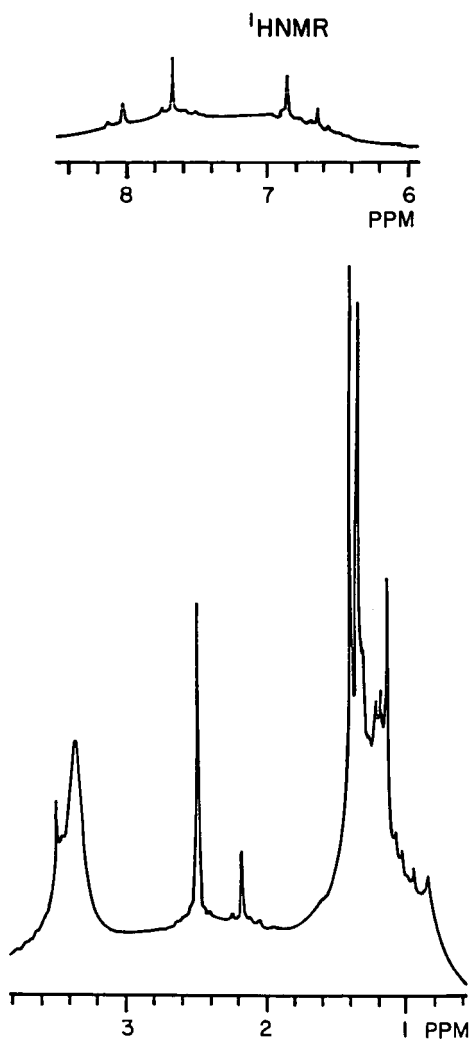
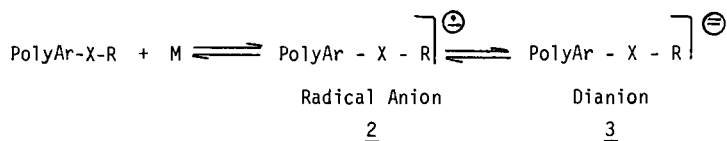


Figure 3.

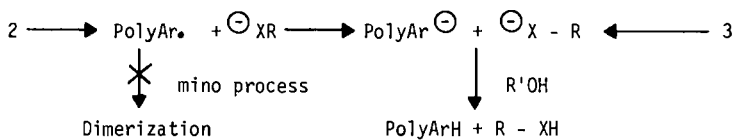


Scheme - 1

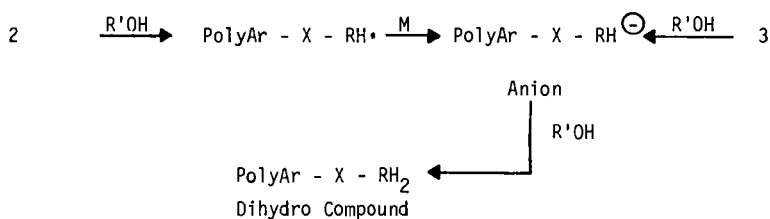


R = Aromatic, Hydroaromatic
 - CH₂Ar, -S Ar
 X = -O, S

CLEAVAGE (Scheme 2)



REDUCTION (Scheme 3)



THE EFFECT OF LIQUEFACTION CONDITIONS ON THE TRACE ELEMENT CONTENT OF SOLUBLE COAL-DERIVED NON-VOLATILE PRODUCT

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INTRODUCTION

Trace element data on coal-derived products at the pilot plant stage are generally available. Several years ago the feed coal (Kentucky hvBb(1) and West Virginia hvAb(2)) and products from a single batch of a long-term liquefaction run on a 400 lb coal/day process development unit were sampled. Preferential removal of selected elements from the liquid product via centrifugation was observed in each case. Iron-containing minerals were preferentially removed if the West Virginia coal was employed; while, aluminum silicates were removed with Kentucky coal. Numerous elements (V, Cr, Mn, Ni, B, Be, Ti, As) did not show preferential removal upon centrifugation. Other elements were predicted to be associated with organic moieties.

Later multi-element analysis data on wet-ashed Amax feed coal, the chloroform-soluble solvent refined coal (Wilsonville, AL demonstration facility) derived therefrom and several size exclusion chromatographic fractions were obtained.(3) Appreciable metal concentration was found in practically all samples. For several elements, concentrations were higher in SRC than in its parent feed coal. This observation suggested the presence of organometallic species since these materials were soluble in a wide variety of organic solvents and had passed 5.0 μ m filters.

Neutron activation analysis has been employed to obtain information on trace elements present in process streams of SRC I and SRC II (Tacoma, WA demonstration facility) products derived from a Western Kentucky coal.(4) In the SRC I process the filtered mineral residue was observed to be the sink for most trace elements with the exception of Ti, Cl, Br and Hg. The SRC I product was found to contain less than 2% of the elemental concentrations in the coal. The SRC II distillate product contained less than 1% of the elemental content of the feed coal. All elements were depleted in SRC I relative to the coal except Br.

A more recent study(5) has been concerned with SRC's which differ (from each other) either in feed coal source, conversion severity or method of residue removal. These materials originated at the Wilsonville facility and were directly analyzed as filtered pyridine solutions via atomic emission spectrometry. Of the metals observed, those which showed any significant concentration (10-1000 μ g/g of SRC) were Al, B, Cu, Fe, Si and Ti. West Kentucky SRC from different mines (Lafayette and Fies) exhibited similar metal content with few exceptions. The effect on elemental concentration of mineral matter removal via filtration or critical solvent deashing was varied. The most significant changes were seen with Ca, Fe, Si and Ti. With the exception of Ti, the elemental concentration in the CSD product was two times or greater than the concentration of the filtered product. An increase in hydrogen pressure (2000-2100 psi) and temperature (418°-450°C) had a minimal effect on metal content. Only for Ca, Si and Ti was there greater than 50% reduction in concentration on going to more severe reaction conditions. Those metals which are expected to be most strongly organo-bound (i.e. transition metals) did not significantly change concentration as a function of processing conditions. Mineral-related elements such as Al, Ca, Mg and Si, on the other hand, appeared to fluctuate

in concentration with processing parameters.

As can be seen above, all trace element studies have involved coal-derived process solvents, pilot plant sampling, lengthy and rather severe reaction conditions and mostly bituminous feed coals. In several of these investigations analytical methods were applied to the ashed sample rather than to the unmodified material where less sample-handling and less opportunity for introduction of impurities are possible.

We wish to report soluble trace metal analysis data on an extensive number of "in-house" short-contact time SRC's prepared with various basic nitrogenous and non-basic model process solvents with both bituminous and subbituminous coals. Data are reported as a function of liquefaction time and temperature, method of residue removal and solvent solubility. In addition, size exclusion chromatography (SEC) of selected SRC's with metal-specific inductively coupled plasma atomic emission spectrometric (ICP-AES) "on-line" detection will be utilized to aid in determining the fate of trace metals during liquefaction.

RESULTS AND DISCUSSION

Trace metal analysis of 18 elements in pyridine via ICP-AES has been performed on numerous in-house SRC's in order to determine the effect of various conversion parameters on metal content. Table I list pyridine soluble SRC (Indiana V coal) metal concentrations as a function of process solvent. In order that some point of reference be established in comparing analyses, concentrations are expressed in μg of metal per gram of extracted moisture-free coal not of SRC. The numbers in each case are representative of two independent liquefaction runs and respective metal determinations. Relative standard deviations varied between 1% and 10% depending on the level of metal. Significant metal content is found for 12 of 18 metals monitored. The highest concentrations invariably are observed with Fe, Si and Ti regardless of the process solvent employed. In general, metal content does not appear to be greatly influenced by the various process solvents employed. Initially, one might have argued that the presence of a good ligand donor solvent such as THQ would complex and solubilize more metal than a poor ligand donor solvent. This is not the case with Indiana V SRC. A greater than ten-fold change in metal content with the four solvent systems is observed only with Ca (17.4-319.9) and Mn (3.73-48.4); while, Al (20.3-121.0) and Si (27.1-208.0) also reflect a rather large fluctuation in concentration. Those elements reflecting the greatest fluctuation in concentration are probably mineral related. Differences in both mineral particle size distribution and viscosity of the SRC extract (which would affect the separation achieved by centrifugation) could cause this variation.

Data were also obtained as a function of reaction time (10 and 30 minutes) for pyridine soluble SRC derived from Wyodak #3 coal. Increased reaction time lowers the content of most metals. Again, many of those elements decreasing in soluble metal concentration with an increase in reaction time could be mineral related (Ca, Mg, Si and Ti). A possible explanation for this observation is that a longer reaction time may more extensively de-complex these elements thereby removing them from the pyridine soluble SRC into the residue. This finding is somewhat surprising in that one might have reasoned that a longer reaction time would lead to more extensive metal solubilization (i.e. mineral matter converting to organometallics). This may very well be the case with Ag, Al, Cu and Fe which show an increase in concentration with reaction time.

The most dramatic change in SRC metal content is found with the extraction solvent employed. Table II compares the analysis of 9 elements obtained on toluene and pyridine soluble fractions (Wyodak #3 SRC). The

TABLE I

METAL ANALYSIS DATA OF SRC'S PREPARED WITH
VARIOUS PROCESS SOLVENTS^{a, b}

Element	TETRALIN/PYRENE (50:50) 86.4% ^c	THQ (100) 93.7% ^c	TETRALIN/MN (50:50) 91.9% ^c	TETRALIN/THO/PYRENE (25:50:25) 92.8% ^c
Al	50.9	107.0	20.3	121.0
B	95.4	97.9	104.0	105.1
Ca	319.9	65.7	17.4	90.4
Cu	10.2	6.87	9.01	5.35
Fe	240.3	165.4	277.4	219.8
Mg	17.9	19.2	6.93	5.35
Mn	21.5	3.73	48.4	13.4
Ni	21.9	19.9	12.4	30.1
Si	132.9	201.4	27.1	208.0
Ti	133.4	113.7	116.2	199.9
V	6.17	5.06	4.82	9.04
Zn	40.8	19.2	15.4	27.3

^aIndiana V Coal; S:C, 2:1, 400°C; 30 minutes; 7.5 MPa H₂

^b<1 µg/g MF Coal measured for Ag, Ba, Cd, Cr, Mo, Sn. Units are µg/gMF coal.

^cPyridine Conversion (MAF)

TABLE II

METAL ANALYSIS DATA OF PYRIDINE AND
TOLUENE SOLUBLE SRC'S^a

Element	WYODAK #3 ^b		INDIANA v ^b	
	Toluene Conversion ^c 77.85%	Pyridine Conversion ^c 82.59%	Toluene Conversion ^c 84.2%	Pyridine Conversion ^c 93.9%
Al	21.5	436.6	6.44	170.1
B	4.56	6.82	40.9	93.7
Ca	18.4	135.2	3.01	90.0
Fe	25.6	207.5	9.58	141.3
Mg	0.81	68.8	0.63	19.7
Ni	1.72	5.63	0.74	6.57
Si	17.9	775.6	16.9	314.5
Ti	15.9	130.0	7.48	43.9
Zn	3.71	8.83	6.74	15.1

^aTHQ; S:C, 2:1; 418°C; 7.5 MPa H₂; 30 minutes

^b<1 µg/g MF Coal: Ag, Ba, Cd, Cr, Mn, Mo, Sn, V (Toluene)
<1 µg/g MF Coal: Cd, Mo, Sn (Pyridine)

^cMAF basis

differences in concentration are large. In many cases metal concentrations are approximately one to two orders of magnitude higher in pyridine soluble SRC relative to toluene soluble SRC. Also, the number of elements appearing at concentrations less than 1 $\mu\text{g/g}$ MF coal are 3 times more numerous for toluene soluble SRC relative to pyridine soluble SRC (9 versus 3) given nearly the same percent conversion. This observation is especially important in that it indicates that the metals concentrate themselves in the toluene insoluble-pyridine soluble products. Again similar findings (Table II) are observed with SRC derived from Indiana V. This finding has an implication regarding metal speciation. The greater concentration of metals in the pyridine soluble fraction suggests that the nature of many of these soluble coal-derived metals is more like a coordination complex rather than a true organometallic metal to carbon bonded species.

Trace metal analysis data are also available for SRC material derived from four different Wyodak coals, Table III. Identical liquefaction conditions were employed. Conversions are based on pyridine solubility which accounts for the relatively high metal contents found. A relatively wide variation (>200%) exists between high and low specific metal content for the four SRC's even though they are all derived from Wyodak coals. The highest metal content appears to be almost uniformly associated with SRC from Wyodak #4 coal (e.g. 13 out of 18 elements). Our Wyodak coals differ considerably from each other in ash content, fixed carbon, %C, %O and %S. Table IV lists ultimate and proximate analyses for these four coal samples. On a moisture free basis the ash content of Wyodak #3 is approximately double the ash content of the other Wyodak coals; yet, its SRC has the lowest metal content for half of the elements monitored. SRC from Wyodak #4 which contains the highest concentration of soluble metals has a feed coal of intermediate ash content and percent sulfur and the lowest percent oxygen. This lack of correlation between ash content and soluble SRC metal content supports the idea of organo-bound metals in coal-derived products. In fact SRC soluble metal content appears to not correlate with either ash, moisture, volatiles nor fixed carbon content. A general trend of metal content versus percent conversion is also not apparent.

Information regarding the number of groups of species for a particular metal and the effective molecular size of each group have been obtained via SEC-ICP-AES on both pyridine and toluene soluble Wyodak #3 SRC (Table II). In both cases the SRC was generated under identical liquefaction conditions. Seven common elements (Ca, Cu, Fe, Mg, Si, Ti, B) were chromatographically detectable in both SRC's employing pyridine elution (e.g. toluene soluble material was re-dissolved in pyridine and eluted from the column with pyridine) and a μ -styragel column. As might have been expected a greater overall concentration of metal is detected in the separation of pyridine soluble SRC than toluene soluble SRC. A greater concentration of larger "sized" material is also observed in pyridine soluble SRC (VR-85) relative to toluene soluble SRC (VR-39) as evidenced by the greater emission intensity of the earlier eluting metal-containing species in the respective metallograms. Totally size-excluded material (retention volume \approx 3.5 mL) as well as selectively permeated metal species are apparent. This implies that there exists a group of organo-metallics of rather large size and another (usually broader) distribution of organometallics of considerably smaller size. This bimodal behavior is especially pronounced in the pyridine soluble fractions.

Metallographic comparison data are available on SRC's prepared at different reaction times. Pyridine extraction was employed; therefore, a greater number of chromatographically detectable metals was realized. Changes in reaction time do not appear to cause as extensive alterations in metal size distribution as changes in reaction temperature. The minor changes which are observed are not consistent from one metal to another. More specifically, B and Ca appear to have a greater concentration of large

TABLE III
METAL ANALYSIS DATA OF SRC'S PREPARED WITH
DIFFERENT WYODAK COALS^{a,c}

Element	Wyodak #1 72.3% ^b	Wyodak #2 84.7% ^b	Wyodak #3 85.4% ^b	Wyodak #4 83.3% ^b
Ag	1.57	-	0.97	5.75
Al	397.0	312.0	194.0	483.0
B	31.8	28.5	14.9	28.6
Ba	3.76	3.27	0.97	15.9
Ca	1567	1228	540.6	4069
Cd	-	-	-	2.02
Cr	1.17	2.35	1.70	4.28
Cu	5.64	4.07	6.92	13.1
Fe	125.0	171.0	157.9	180.0
Mg	391.0	258.0	90.5	320.0
Mn	19.6	21.9	7.12	17.0
Mo	-	-	-	4.35
Ni	13.8	17.6	20.6	53.0
Si	113.0	170.0	104.5	169.0
Sn	-	-	-	-
Ti	49.0	44.2	39.5	66.9
V	4.28	4.34	5.28	7.10
Zn	11.6	22.1	9.43	52.7

^a50% tetralin/50% methyl naphthalene; S:C, 2:1; 400°C; 7.5 MPa H₂;
30 minutes.

^bPyridine conversion (MAF)

^cUnits are µg/g of MF coal

TABLE IV
ULTIMATE AND PROXIMATE ANALYSES

	Wyodak ^a #1	Wyodak ^a #2	Wyodak ^a #3	Wyodak ^a #4	Ind V ^c
%C	65.81	64.00	48.27	64.80	65.8
%H	5.15	5.34	4.47	5.59	5.0
%N	0.86	0.85	0.71	0.88	1.4
%O	21.19	20.97	24.32	17.52	7.6
%S	0.41	1.07	6.60	1.96	3.7
Ash	5.1	5.9	20.3	0.1	10.3
Moisture	9.9	8.1	7.0	7.6	5.1
Volatiles	36.1	37.7	35.0	39.4	37.4
	(54.8)	(52.6)	(37.0)	(48.6)	
Fixed Carbon	49.3	48.3	37.7	44.9	47.2
	(40.1)	(41.0)	(41.4)	(42.6)	

^aSamples prepared by drying for 5 days, 133 Pa, 20°C to remove storage water.

^bNumbers in parenthesis are proximate analyses on moisture free basis
obtained in our laboratory.

^cData obtained from Kerr McGee Corp., Crescent, OK.

size species at the longer reaction time (30 minutes) than the shorter one (10 minutes). The reverse situation operates with Cu, Fe, Ti and Zn. An interpretation of these results suggest that B and Ca may incorporate with initial regressive reaction products; whereas Cu, Fe, Ti and Zn are tied-up more with the progressive reaction products. A longer reaction time should be conducive to both primary-secondary product progressive reactions as well as to regressive reaction behavior.

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ANALYTICAL CHEMISTRY OF PRODUCTS FROM PROCESS STRATEGIES DESIGNED TO REDUCE THE BIOLOGICAL ACTIVITY OF DIRECT COAL LIQUEFACTION MATERIALS

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INTRODUCTION

The current status of understanding the chemical basis for the generally increased genetic activity of direct coal liquefaction materials, as compared to petroleum-derived products, has led to the investigation of a number of potential process strategies for reducing the biological activities of coal-derived liquids. Approaches that have been investigated include optimized fractional distillation, catalytic hydrotreatment, recycling of heavy-end and bottoms materials, and two stage liquefaction coupled with reduced liquefaction severity and improved quality hydrogen donor solvents.

Biodirected chemical analyses of coal liquefaction materials over the last several years have led to the identification of at least two important classes of compounds which are largely responsible for the biological response observed in laboratory systems upon exposure to these materials. The classical carcinogens in coal liquids are the polycyclic aromatic hydrocarbons (PAH), primarily those having from 4 to 6 aromatic rings. Kennaway, Cook and others in the early part of this century showed that certain coal-derived PAH could cause skin tumors in mice and rabbits (1,2,3). It has been found, in general, that genetic activity, particularly initiation of tumorigenesis, resides in high boiling heavy-end materials and correlates with overall PAH content better than with any other chemical class (4-6). More recently nitrogen-containing polycyclic aromatic compounds (N-PAC), specifically the amino-PAH, have been recognized as genotoxic constituents in several coal-derived materials. In quantitative terms, the amino-PAH occur at relatively lower concentrations as compared to the PAH. However, due to the increased sensitivity of the Salmonella typhimurium microbial mutagenicity test to amino-PAH, they are readily detected in the complex coal liquid mixtures by this biological assay (7-11). The possible contribution of amino-PAH to the etiology of any cancers induced in coal product workers is only now beginning to be understood. Amino-PAH such as 2-aminonaphthalene and 4-aminobiphenyl are recognized as human carcinogens (12). Furthermore, recent studies have demonstrated that the amino-PAH as a chemical class do contribute to the overall initiation of skin tumors in laboratory mice (13).

A common goal of the direct liquefaction process strategies considered in this study is the reduction of biological activity via reducing the concentration levels of the amino-PAH and the 4-, 5- and 6-ring PAH. In this report, coal liquefaction strategies such as distillation, bottoms recycle, hydrogenation, and two stage liquefaction will be discussed in terms of their effect on the chemical composition of process materials.

ANALYTICAL METHODS

The evolution and development of analytical methods at PNL (Pacific Northwest Laboratories) has been primarily directed by the requirement of determining the biologically adverse chemical classes and compounds in coal liquefaction materials. Accordingly, methods have been designed for the identification and quantification of not only homogeneous chemical classes, but also individual components. Figure 1 outlines the overall analytical approach currently used. An

initial separation of crude materials by adsorption column chromatography (14) enables the determination of gross chemical composition in terms of PAH and N-PAC content. Secondary chromatographic separations are achieved by HPLC methods (15) for the PAH, and a combination of adsorption and gel permeation chromatography (14,16) for the N-PAC. Finally, instrumental methods such as capillary column gas chromatography and mass spectrometry are used to provide detailed qualitative and quantitative chemical analysis of individual components in the separated materials.

During the last several years, the SRC (solvent refined coal) processes have received prime attention and consideration as potential direct coal liquefaction technologies. An illustration of the detailed data obtained from the previously described analytical procedures for the PAH fraction of a full boiling range SRC II end-product is provided in Figure 2 and Table 1. It should be noted at this point that all process materials investigated during this study and discussed in this paper were from process development units or pilot plants and may not necessarily be representative of products which will eventually be produced on a commercial scale.

RESULTS AND DISCUSSION

DISTILLATION

An effective process technique that has been used in the petroleum industry for the gross separation of end-products of refining according to volatility is distillation. Optimized fractional distillation has recently been applied to the products of direct coal liquefaction in an effort to effect a molecular weight separation and isolate the biologically active components in the higher boiling fractions (6). Bioassays of crude distillates and chemical class fractions from several direct liquefaction processes have shown that the majority (>99%) of genetic activity is contained in the distillate fractions boiling above 700°F (4-5). Figures 3 and 4 aid in understanding the chemical basis for this observation.

Figure 3A and 3B present chemical class weight distribution information for the 50°F distillate cuts of typical end-products from the SRC II and EDS (Exxon Donor Solvent) coal liquefaction processes, respectively. For each process, greater than approximately 80% of the material is distilled below 700°F. In terms of chemical class composition, there is a decrease in aliphatic hydrocarbon content and increasing levels of N-PAC and polar hydroxylated polycyclic aromatic hydrocarbons (HO-PAH) with increasing boiling point temperature. The neutral PAH portion of each distillate cut generally remains constant.

The effect of distillation temperature on molecular weight is shown in Figure 4 for the PAH fraction of the SRC II boiling point cuts. As a general trend, compounds of increasing molecular weight can be correlated with increasing distillation temperature. For example, pyrene, which is noncarcinogenic, is at a maximum concentration in the 700-750°F cut, while the potent carcinogenic compounds such as benzo(a)pyrene are distilled in the greater than 800°F cuts. This trend is also observed for the mutagenic N-PAC and amino-PAH components of the distillate fractions.

In summary, optimized fractional distillation in effect eliminates the bulk of components from the full boiling range material (Figure 1) which have a molecular weight greater than approximately 200 daltons and minimizes the levels of compounds that contain polar nitrogen and oxygen functional groups. Additionally, materials resulting from this process strategy would have a higher aliphatic hydrocarbon content and would be nominally biologically inactive.

BOTTOMS RECYCLE

Information from the distillation studies led to the suggestion that the greater than 700°F material, or bottoms, might simply be recycled continuously to extinction within the process to yield a non-biologically active end-product. Recently, experiments have been conducted with the SRC II process by the Merriam Coal Liquefaction Laboratory to determine the feasibility and applicability of this process strategy. Crude materials sampled from the SRC II process while operating in the bottoms recycle mode, with a recycle cut point temperature of 290°C (554°F) and assayed for microbial mutagenicity (*S. Typhimurium*, TA98) showed no detectable activity although these net products contained 5-10% (by weight) material boiling above the recycle cut point temperature. This work also demonstrated that an increased recycle of heavier-ends reduced the net yield of heavy distillate.

CATALYTIC HYDROGENATION

Catalytic hydrogenation has been considered both as an off-line post-production upgrading step, as well as an integral process in direct coal liquefaction technologies. Early results with catalytic hydrotreatment of an SRC II fuel oil blend material showed that mutagenic activity was substantially reduced by hydrogenation (17). This was explained by the reduced levels of amino-PAH due to deamination of the nitrogen functionality which occurs readily under the reducing conditions of hydrogenation processes. Furthermore, hydrogenation of the PAH components can lead to reduced aromaticity and/or carbon-carbon bond scission of higher molecular weight PAH. This again leads to a reduction in the biological potency of the end-products.

Several direct liquefaction technologies including EDS and TSL (two stage liquefaction) incorporate some form of catalytic hydrogenation step within the process. Table 2 lists the quantitative results for the major components detected in the PAH fraction of the 700-750°F distillate cut of end-products from the SRC II (no hydrogenation) and EDS (process solvent hydrogenation) processes. An obvious effect of the hydrogenation process is a general reduction in the EDS material of the concentration levels of parent PAH, for example pyrene and benzofluorene, as compared to other constituents of the fraction such as the hydroaromatics and alkylated species. In general, the EDS distillate cut is composed of several compounds within a fairly narrow concentration range, while the SRC II material has a few major components with other constituents at much lower concentration levels. Table 3 gives an estimate of the magnitude of the chemical differences that result from the hydrogenation process. The increased proportions of alkylated and hydroaromatic PAH in hydrotreated materials has the net effect of increasing the hydrogen to carbon ratio and enhancing the quality of both process products and recycle solvents.

TWO STAGE LIQUEFACTION

Two stage liquefaction processes such as the second generation integrated two stage liquefaction (ITSL) incorporate several process features which lead to both process streams and potential product materials which show reduced genotoxicity (18,19). It appears that the two most important features are reduced liquefaction severity in the first stage and catalytic hydrotreatment in the second stage. Low severity extraction depends upon the availability of high quality hydrogen-rich solvent which results from hydrotreatment. Severity in the initial liquefaction step is reduced primarily by lowering the residence time of the coal slurry in the first stage reactor. The improved solvation and hydrogenation properties of the higher quality solvent allows the coal to be solvated quickly and efficiently, thus minimizing the possibility of retrograde reaction which leads to the formation of polar materials and may cause polymerization or coking.

Reduction in nitrogen content of the distillates is the main reason for the lower genotoxicity of the ITSL materials as compared to the single stage processes. Figure 6 compares gas chromatograms of the nitrogen-containing PAH fractions after the first and second stages of the ITSL process. Deamination that is only partial in the low severity reactor is relatively complete in the hydrotreater product. This reduces the overall concentration of genotoxic amino-PAH in the process material and end-products. Similarly, hydrogenation and cracking occurs for the other PAH components in the process material resulting in the superior recycle solvent properties required for low severity liquefaction in the first stage and high quality end-products that are suitable for upgrading and refining.

CONCLUSION

The ability to perform detailed chemical analysis provides insights and understanding into both the areas of biological effects and process strategies. There are a number of chemical differences which have been discussed for the different products from direct liquefaction strategies, including hydrogenation, de-nitrogenation, and alkylation. The higher molecular weight genotoxic PAH and N-PAC which are minor constituents in most full range distillate coal liquids can be effectively reduced in concentration by optimized fractional distillation, bottoms recycle, or hydrogenation. Furthermore, two stage liquefaction with enhanced recycle solvents under low severity conditions coupled with hydrogenation reduces the aromatic and polar PAH content while increasing the hydrogen to carbon ratio of the process material. In general, the strategies investigated in this work result in higher quality process materials and end-products which are suitable either for refining or upgrading into usable products.

ACKNOWLEDGEMENT

This work was supported by the U.S. Department of Energy, Contract No. DE-AC06-76RLO 1830 with the Office of Fossil Energy.

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TABLE 1. Quantitative and Qualitative Analysis of the PAH in the SRC II Full Range Distillate(a)

Peak No.	Mol. Wt.(b)	Compound Identification	PAH Fraction (PPM (ug/g))(c)
1	128	Naphthalene	730 ± 50 ^(d)
2	142	2-Methylnaphthalene	15,040 ± 680
3	156	1-Methylnaphthalene	2,840 ± 130
4	156	2-Ethyl-naphthalene	11,400 ± 540
5	156	2,6- and/or 2,7-Dimethylnaphthalene	12,500 ± 1000
6	156	1,7- and 1,6- or 1,3-Dimethylnaphthalene	8,260 ± 440
7	152	C ₂ -Naphthalene	
8	154	Acenaphthylene	340 ± 20
9	170	Acenaphthene	7,990 ± 450
10	170	C ₂ -Naphthalene	
11	168	C ₂ -Naphthalene	
12	166	Dibenzofuran	13,360 ± 740
13	166	Fluorene	13,960 ± 1180
14	168	C ₁ -Acenaphthene and/or Dihydrofluorene	39,960 ± 4140
15	184	C ₂ -Naphthalene	
16	180	9-Methylfluorene	16,650 ± 3040
17	182	C ₁ -Dibenzofuran and/or C ₂ -Acenaphthene and/or C ₁ -Dihydrofluorene	
18	180	2-Methylfluorene	11,750 ± 680
19	180	1-Methylfluorene	9,830 ± 480
20	180,182,198	C ₁ -Fluorene and/or C ₂ -Acenaphthene and/or C ₁ -Dihydrofluorene, and/or C ₁ -Dibenzofuran	
21	184	Dibenzothiophene	12,290 ± 750
22	196	C ₂ -Acenaphthene and/or C ₂ -Dihydrofluorene	
23	178	Phenanthrene	44,640 ± 2840
24	194,196	C ₂ -Fluorene and/or C ₂ -Dihydrofluorene	
25	196	C ₂ -Dihydrofluorene	
26	192	3-Methylphenanthrene	9,300 ± 840
27	192	2-Methylphenanthrene	11,950 ± 800
28	192	1-Methylphenanthrene	3,680 ± 490
29	212	2-Chloroanthracene Internal Standard	
30	204	Dihydrofluoranthene	8,780 ± 100
31	202	Fluoranthene	3,820 ± 30
32	202	Pyrene	19,520 ± 470
33	204	Dihidropyrene	
34	218	C ₁ -Dihydrofluoranthene and/or Benzo(a)naphthofuran	
35	216	Benzo(a)fluorene	2,840 ± 230
36	216	Benzo(b)fluorene and/or 2- or 4-methylpyrene	10,360 ± 1110
37	218	Dihydrobenzo(b)fluorene and/or Benzo(b)naphthofuran	
38	216	1-Methylpyrene	2,650 ± 470
39	230	C ₁ -Benzofluorene and/or C ₂ -pyrene/fluoranthene	
40	228	BenZ(a)anthracene	660 ± 60
41	228	Chrysene	1,110 ± 120
42	242	6- or 4-Methylchrysene	2,110 ± 210
43	252	Benzo(j or b)fluoranthene	250 ± 50
44	252	Benzo(e)pyrene	200 ± 60

(a) SRC II Full Range Distillate obtained from Gulf Research and Development Co., Merrian Coal Liquefaction Laboratory, Shawnee Mission, KS. An Amax Belle Ayr Mine subbituminous coal was used during run DOE 454RA which was made in the convention recycle mode.

(b) As determined by capillary column gas chromatographic-mass spectrometry.

(c) Determined from response factors of standard compounds.

(d) Based on three determinations; 10 mg/ml, 5 mg/ml, and 2.5 mg/ml dilutions.

TABLE 2. Concentrations of the Major Components of the 700-750°F Distillate Fractions of SRC II and EDS End-Products.

Compound	PAH FRACTION PPM (µg/g) ^(a)	
	E.D.S. ^(b)	SRC II ^(c)
Dihydrofluoranthene	2,098 ± 36	21,822 ± 6,335
Fluoranthene	1,089 ± 16	30,210 ± 1,819
Pyrene	29,838 ± 976	275,991 ± 32,372
Dihdropyrene	6,391 ± 157	27,733 ± 8,413
Benzo(b)fluorene and/or 2- or 4-Methylpyrene	47,042 ± 11,610	257,629 ± 70,359
1-Methylpyrene	26,567 ± 6,371	34,335 ± 4,405
Benz(a)anthracene	308 ± 23	4,098 ± 942
Chrysene	1,554 ± 335	2,086 ± 561

- (a) Concentration of components in the PAH fraction as determined from response factors of standards. Based on three determinations at 10 mg/mL, 5mg/mL, 2.5 mg/mL dilutions.
- (b) EDS 50° distillate from a feed blend of naptha and process solvent of Illinois No. 6 coal; ECLP operations, Exxon Research and Engineering Co., Baytown, TX.
- (c) SRC II 50° distillates from a feed blend of naptha and process solvent of Powhatan No. 5 mine coal; PDU P-99 operated by Gulf Science and Technology Co., Harmarville, PA.

TABLE 3. Concentration Ratios of Selected 4-Ring PAH in the 700-750°F Distillate Fractions of SRC II and EDS

Compound Ratio	EDS	SRC II
<u>pyrene</u> 1-methylpyrene	1.1	8.0
<u>pyrene</u> dihdropyrene	4.7	10.0
<u>fluoranthene</u> dihydrofluoranthene	0.5	0.7

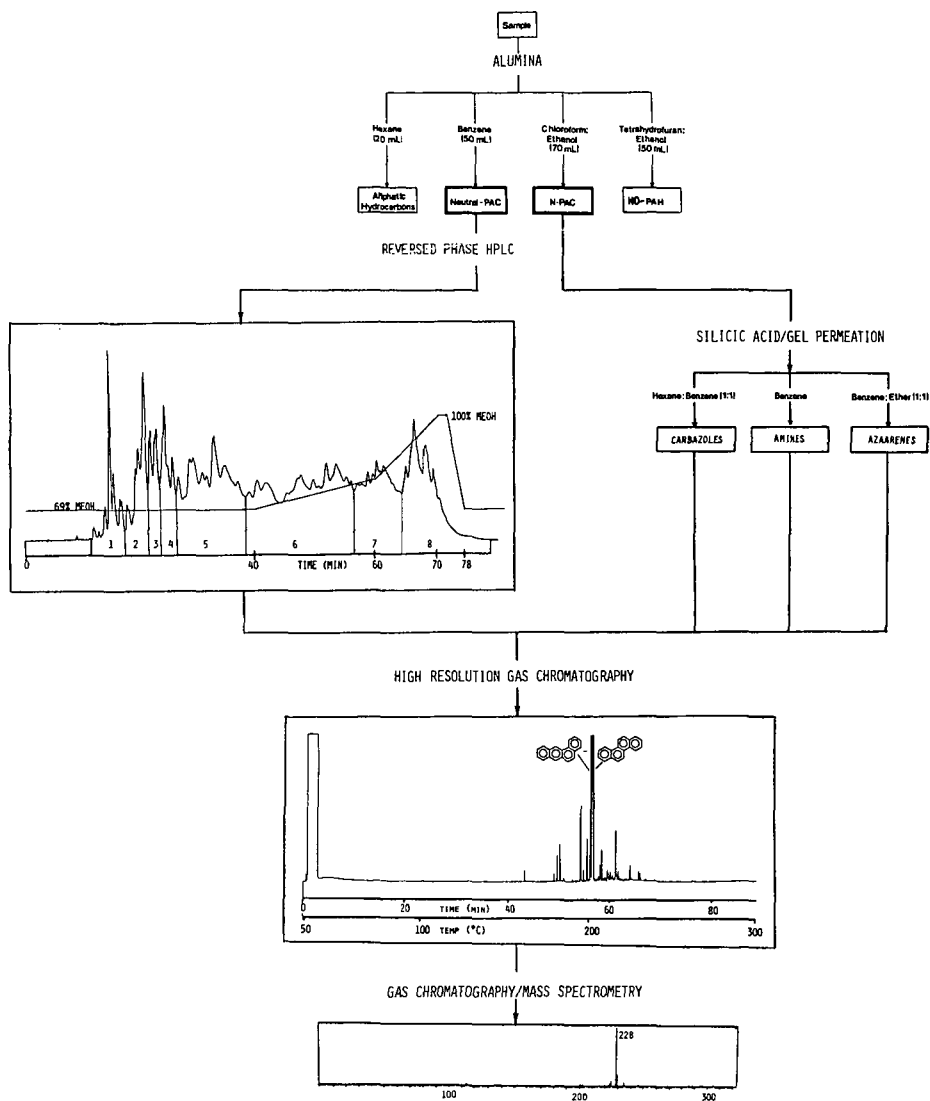


FIGURE 1. Overview of the analytical methodology used for the detailed chemical characterization of coal liquefaction materials.

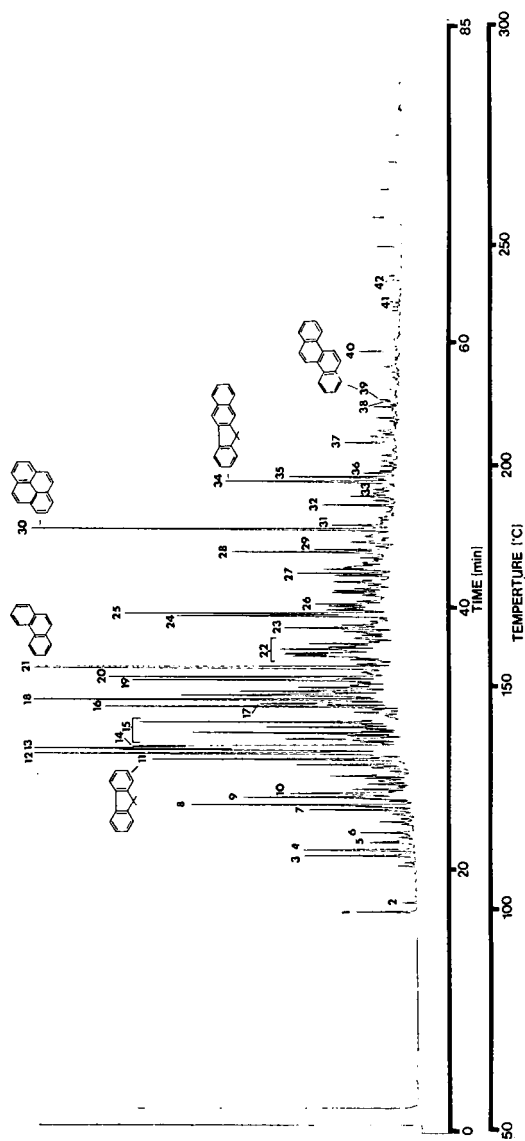


FIGURE 2. Capillary column gas chromatogram of the PAH fraction from SRC II full boiling range material. Peak numbers refer to compounds listed in Table I. Conditions: 30 m x 0.25 mm Durabond 5 (J & W Scientific) fused silica column, temperature programmed from 50°C to 280°C at 4°C/min.

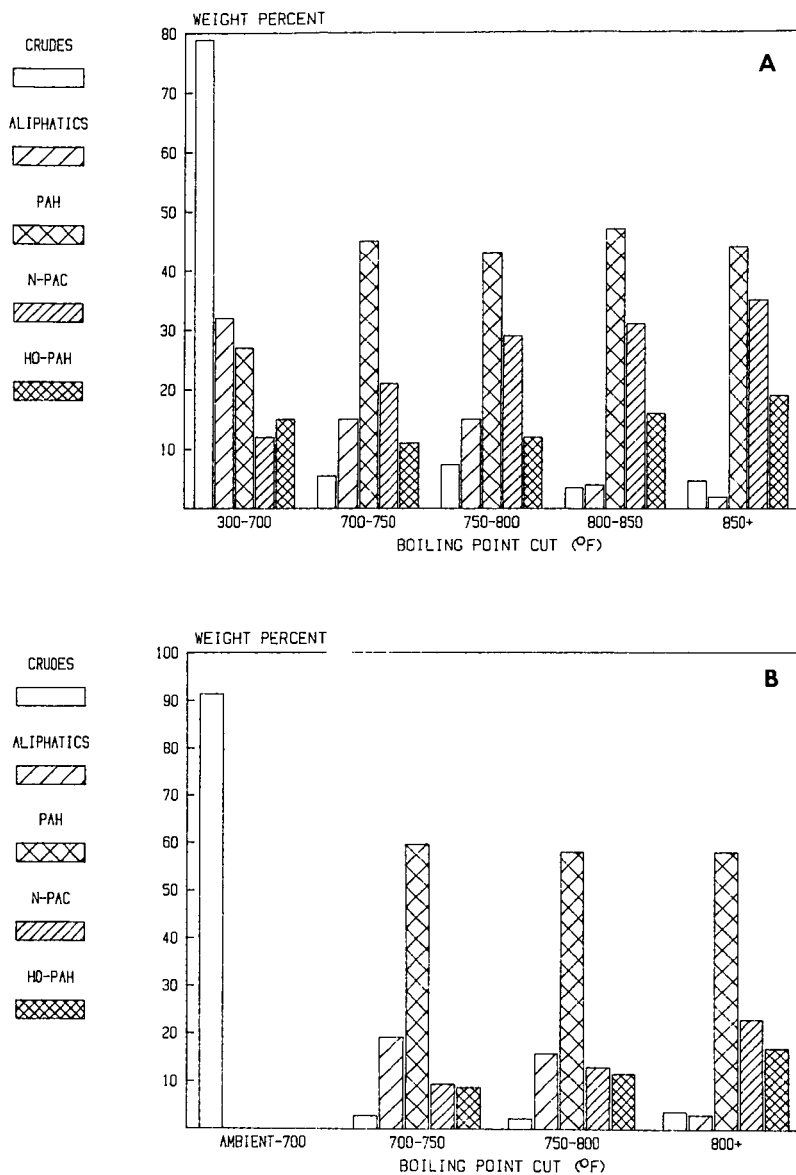


FIGURE 3. Weight distribution of chemical classes in the (A) SRC II and (B) EDS distillate fractions (see Table 2 footnotes for a detailed description of these process materials).

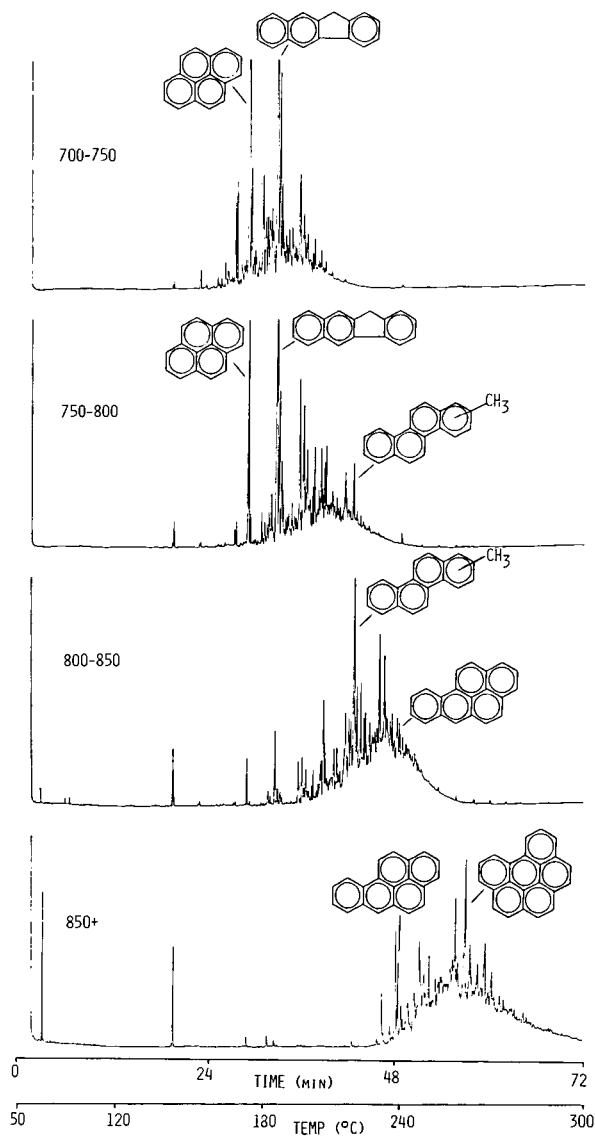


FIGURE 4. Capillary column gas chromatograms of the PAH fractions from the SRC II 50°F distillates fractions. (See Table 2 footnotes for a detailed description of this coal-derived material.) Conditions as in Figure 2.

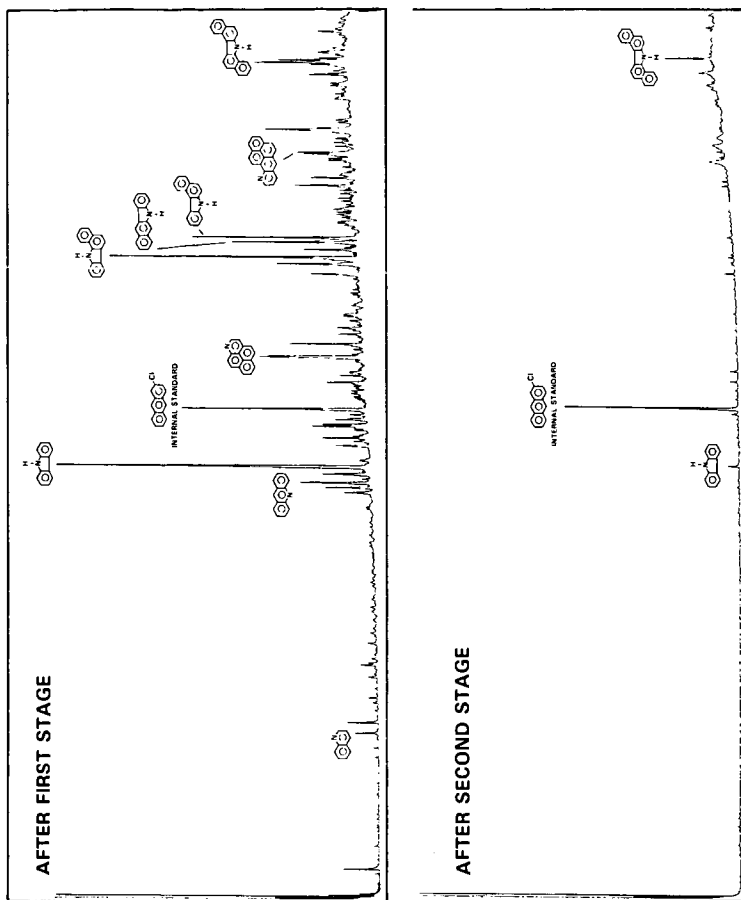


FIGURE 5. Process effects on the N-PAC content of two stage liquefaction products. Gas chromatographic condition as in Figure 2. Samples were from the ITSL process development unit operated by C. E. Lummus, New Brunswick, NJ.